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# Synthesis, Elemental Analysis, and Metallographic Preparation of Lithium (Li)-Silicon (Si) Alloys

**by Joshua B. Ratchford, Bruce A. Poese, Cynthia A. Lundgren, Jan L. Allen, and Jeff Wolfenstine**

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We report methods used to synthesize and prepare $Li_{12}Si_7$ and $Li_{22}Si_5$ for nanoindentation testing. The alloys were made by heating lithium granules with silicon powder. X-ray diffraction, inductively coupled plasma-mass spectrometry, and optical microscopy confirmed that the alloys were single phase. Optical microscopy showed that the alloys were fully dense.

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# 1. Introduction

Recently, lithium (Li)-silicon (Si) alloy anodes have been considered as attractive alternatives to graphite anodes in Li-ion batteries, because the specific capacities of these alloys are from four (1620 $mAhg^{-1}$, $Li_{12}Si_7$) to 10 times (4200 $mAhg^{-1}$, $Li_{22}Si_5$) greater than graphite (*1–4*). Unfortunately, these capacities diminish with cycling because substantial volume changes during Li-ion addition/removal cause decrepitation. It has been proposed that knowledge of the elastic properties of these alloys, like Young's modulus, can be used to develop models that can predict and prevent decrepitation of Li-Si alloys (*5, 6*). Several groups recently predicted values of the elastic properties of these alloys using density functional theory (*5, 7, 8*). Experimental data to verify these values did not exist until our group's recent publication of Young's modulus for $Li_{22}Si_5$ that was measured using nanoindentation testing (*9*). We have also recently measured Young's modulus for $Li_{12}Si_7$ using the same methods (*10*). We believe that the methods used for our work with $Li_{12}Si_7$ and $Li_{22}Si_5$ will be helpful to other researchers who wish to synthesize, study the microstructure, and measure the mechanical properties of Li alloys using nanoindentation testing. Therefore, the objective of this report is to document (1) the method used to synthesize $Li_{12}Si_7$ and $Li_{22}Si_5$, (2) the methods we used to determine the weight percent of lithium of these alloys using inductively coupled plasma mass spectrometry (ICP-MS), and (3) the metallographic methods we used to prepare the surfaces of these alloys for microstructural analysis and nanoindentation testing.

# 2. Experimental

## 2.1 Synthesis

All procedures used to synthesize $Li_{12}Si_7$ and $Li_{22}Si_5$ were performed in a glove box (VAC Nexus One®) filled with argon, which contained less than 1 ppm of oxygen and 1 ppm of water. In order to synthesize $Li_{12}Si_7$, 1.490 g of lithium granules (Alfa Aesar) was mixed with 3.510 g of silicon powder (Alfa Aesar). In order to synthesize $Li_{22}Si_5$, 2.605 g of lithium granules were mixed with 2.395 g of silicon powder. The mixtures of the Li granules and Si powder were pressed into pellets using stainless steel dies. The pellets were heated inside molybdenum crucibles using a muffle furnace. The Li-Si phase diagram shows that $Li_{12}Si_7$ and $Li_{22}Si_5$ melt at 690 °C ($T_m$ = 963 K) (*11*). We found that samples heated to 800 °C showed improved phase purity as compared to those heated at 690 °C. Therefore, the samples were heated from 20 to 800 °C over the course of 40 min and then at 800 °C for an additional 30 min. The samples were then heated at 450 °C for 16 h to ensure their homogeneity before it was slowly cooled to 20 °C.

## 2.2 X-ray Diffraction Parameters

To determine the phase purity of $Li_{12}Si_7$ and $Li_{22}Si_5$, approximately 100 mg of the samples were removed from the center of the crucibles, ground into fine powders, and placed upon a glass slides for analysis by x-ray diffraction. Because these alloys are sensitive to ambient moisture, the samples were hermetically sealed with Kapton® film before these were immediately transferred from the dry box to the x-ray diffractometer (Rigaku Ultima III®). A Cu-Kα emission source and the Bragg-Brentano geometry was used to obtain a diffraction pattern from 15° to 80° two-theta with a step size of 0.02º two-theta at a scan rate of 1° two-theta per minute.

## 2.3 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Inductively coupled plasma-mass spectrometry (PerkinElmer ELAN® ICP-MS) was used to confirm the weight percentage of lithium in the alloys. For $Li_{12}Si_7$ and $Li_{22}Si_5$, 100-mg powder samples were dissolved in solutions composed of 6 ml of 50 wt.% hydrofluoric acid (Fisher) and 3 ml of 70 wt.% nitric acid (Fisher) for 12 h in a Teflon® container. We wish to emphasize that extra caution was used to prepare these samples for ICP-MS because both alloys are very reactive with water. The sample solutions were then diluted to 100 g with a solution composed of 0.1 wt.% nitric acid and 0.3 wt.% hydrofluoric acid. $^7Li^+$ detection with the spectrometer was standardized with solutions made by diluting a 10-μg/ml atomic absorption standard solution with a 0.1 wt.% nitric acid and 0.3 wt.% hydrofluoric acid solution at 10, 100, and 1000 times. Linear regression analysis of the $^7Li^+$ intensities measured from these standard solutions were used to generate the following calibration curve:

$$I_{Li} = 92.4\times10^3 C_{Li} + 4.0\times10^3 \quad (1)$$

where $I_{Li}$ is the measured intensity of $^7Li^+$ and $C_{Li}$ is the concentration of lithium in solution. $^7Li^+$ detection with the spectrometer was linear over four orders of magnitude. The measured intensity of $^7Li^+$ in the sample solution was substituted into equation 1 to determine the concentration of lithium, $C_{Li}$, in the dissolved $Li_{12}Si_7$ and $Li_{22}Si_5$ sample solutions.

## 2.4 Metallographic Preparation of Alloys

To prepare samples of $Li_{12}Si_7$ and $Li_{22}Si_5$ for mechanical testing, granules of the samples were cold mounted in epoxy (Buehler EPO-KWICK®)*. Granules were rough polished with 320-, 400-, and 600-grit abrasive papers (Buehler BuehlerMet®II) in series. Because the alloy is water reactive, the papers were lubricated with mineral oil instead of water. Suspensions of alumina powders (Buehler) in mineral oil were used to fine polish the granules against a microfiber cloth (Buehler MicroCloth® PSA). Alumina powders with diameters of 1.0, 0.3, and 0.05 μm were used in series. The surfaces of the granules were fine polished until a mirror finish was obtained. The homogeneity of the fine polished surface was confirmed by examination with optical microscopy. To determine the grain size of the alloy, the polished surfaces were etched for

*A stainless steel washer was used to hold the granules against the bottom surface of the mold as the liquid epoxy hardened.

several seconds with a solution that was 0.2% by mass water and 0.3% by mass hydrochloric acid diluted with hexane. Etching was quenched by immersing the sample into mineral oil. The grain size was measured from optical images of the etched surface using the linear intercept method (*12*).

## 3. Results and Discussion

### 3.1 Phase Composition of Synthesized Alloys

The x-ray diffraction patterns in figure 1a for $Li_{12}Si_7$ and figure 1b for $Li_{22}Si_5$ show that the alloys are polycrystalline. The amorphous background in the 15–30° range of figure 1b is an artifact of the Kapton tape. The position of the diffraction peaks that match those from the International Centre of Diffraction Data's powder diffraction file for $Li_{12}Si_7$ (PDF# 00-040-0942) and $Li_{22}Si_5$ (PDF# 01-073-2049) are marked with bullets. Figure 1 shows that the positions of the diffraction peaks from the alloys agree perfectly with those from the powder diffraction files. Impurity peaks are marked with crossbars in figure 1a. These correspond to the (311) diffraction peak of $Mo_4O_{11}$ (PDF# 01-089-6725) and the (111) diffraction peak of $MoSi_2$ (PDF# 01-081-0167). These results suggest that the synthesized $Li_{12}Si_7$ is mainly single phase $Li_{12}Si_7$ with a small amount of second phase $Mo_4O_{11}$ and $MoSi_2$ impurities. No impurity peaks are observed in figure 1b. These results suggest that the synthesized $Li_{22}Si_5$ alloy is single phase $Li_{22}Si_5$.

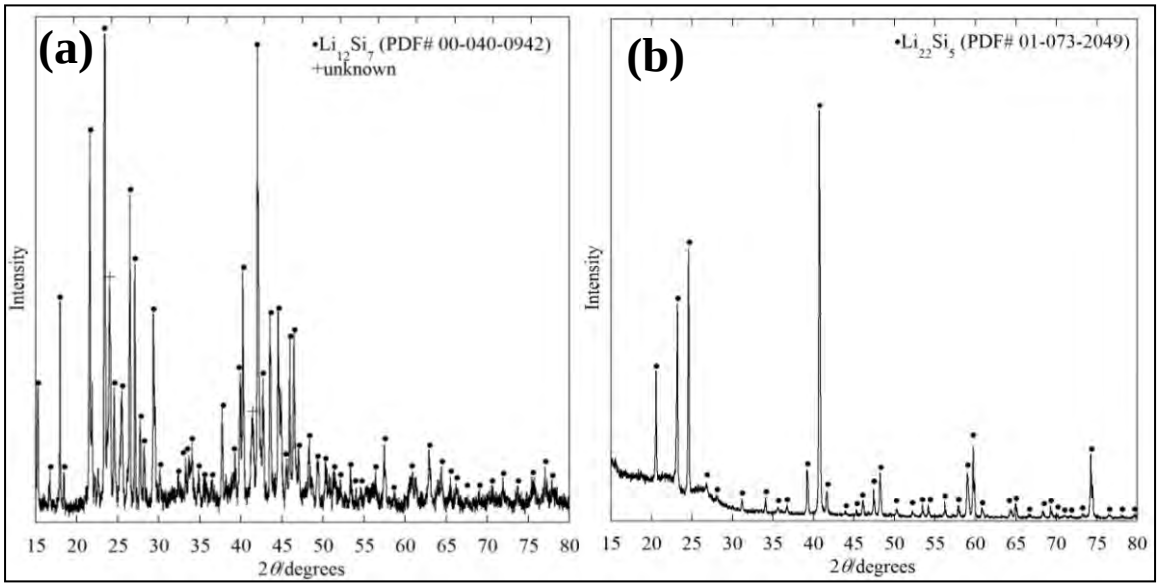


Figure 1. X-ray diffraction patterns produced from powder samples of (a) $Li_{12}Si_7$ and (b) $Li_{22}Si_5$.

### 3.2 Elemental Analysis

Table 1 shows the measured weight percentages of lithium in the $Li_{12}Si_7$ and $Li_{22}Si_5$ obtained using ICP-MS, and the expected weight percentage of lithium in these alloys from the Li-Si phase diagram. As table 1 shows, the measured weight percentage of lithium in the alloys agrees with the expected weight percentage of lithium from the Li-Si phase diagram. These results further confirm that the synthesized alloys are indeed single phase $Li_{12}Si_7$ and $Li_{22}Si_5$. Because molybdenum impurities were observed in the x-ray diffraction patterns obtained from the $Li_{12}Si_7$ samples, the weight percentage of molybdenum in this alloy was also measured. Table 1 shows that the weight percentage of molybdenum in this alloys was 1.8±0.5 wt.%. In the worst case, the alloy is 2.3% by mass molybdenum. From this mass composition in conjunction with the densities of the impurities, the $Li_{12}Si_7$ alloy is at most 0.4 %.vol $MoSi_2$ or 0.5 %.vol $Mo_4O_{11}$—a negligible volume fraction to consider for a weighted average of mechanical properties for mixed phases of materials. From this result, we conclude that the mechanical properties measured from the synthesized $Li_{12}Si_7$ will represent the true materials properties of $Li_{12}Si_7$.

Table 1. Elemental composition of $Li_{12}Si_7$ and $Li_{22}Si_5$ determined by ICP-MS.

| **Alloy** | **Expected Li wt.%**[a] | **Li wt.%** | **Mo wt.%** |
|---|---|---|---|
| $Li_{12}Si_7$ | 29.8 | 28.6±1.5 | 1.8±0.5 |
| $Li_{22}Si_5$ | 52.1 | 52.5±1.1 | – |

[a]Okamoto, H. *Journal of Phase Equilibria and Diffusion* 30, 2009, 118–119.

### 3.3 Microstructural Analysis

Optical microscopy showed that the $Li_{12}Si_7$ and $Li_{22}Si_5$ microstructures were homogeneous over the entire polished area of the granule. Each alloy is fully dense with no porosity and no second phases show (figure 2). In addition, figure 2 shows that the grain structure of $Li_{12}Si_7$ and $Li_{22}Si_5$ are fairly equiaxed, with grain sizes of 4±1 and 25±3 μm, respectively.

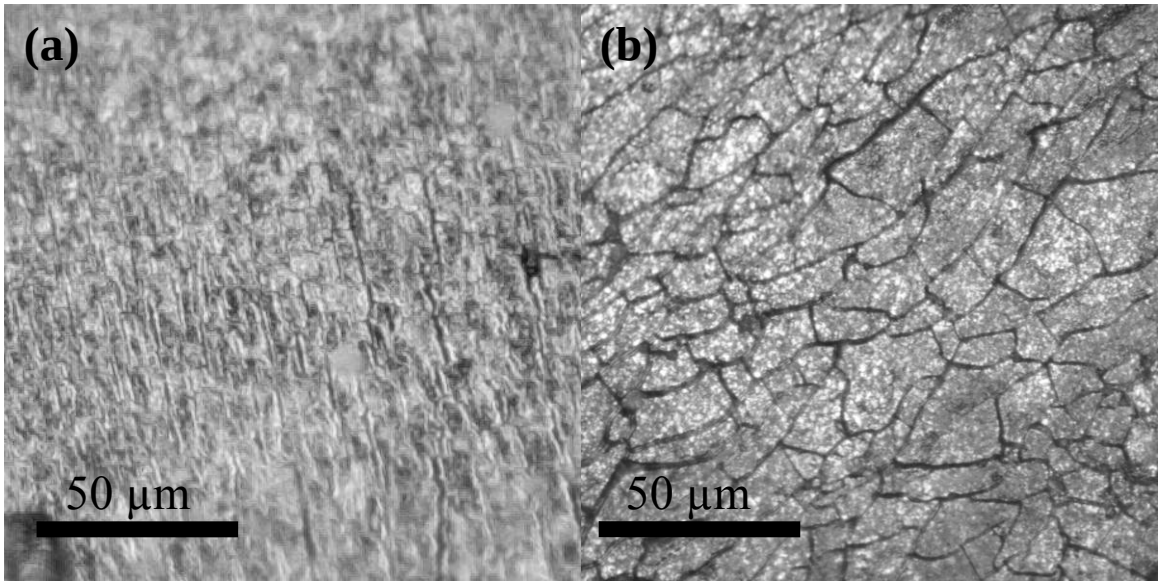


Figure 2. Optical images of etched samples (a) $Li_{12}Si_7$ and (b) $Li_{22}Si_5$.

## 4. Conclusion

A method to synthesize and prepare the Li-Si alloys, $Li_{12}Si_7$ and $Li_{22}Si_5$, for mechanical testing was developed. Analysis of these alloys using x-ray diffraction and ICP-MS showed that the alloys were single phase $Li_{12}Si_7$ and $Li_{22}Si_5$. Optical microscopy confirmed the homogeneity of the microstructure of each alloy.

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